

APPLICATION OF AN AUTOMATED CLEANUP SYSTEM FOR THE ANALYSIS OF PCDD/PCDF IN ENVIRONMENTAL SAMPLES

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Introduction

At present, there is ample evidence that chlorinated aromatic compounds with a dioxin-like activity have an adverse effect on exposed metabolisms. Stringent regulations governing public health reflect the widespread interest in this field and at present, dioxin analyses are the most reliable of existing assays of chemical substances. The growing demand for fast laboratory measurements should not constitute a pretext for lowering the quality of the analyses. Experience shows that to guarantee good quality data appropriate methods and techniques as well as quality control (QC) measures are required. The extract analyses by HRGC/HRMS using isotopic dilution as a quantification method and operating in a SIM mode are suitable for dioxin determinations. However, the cleanup process is a crucial step before carrying out these analyses.

The Power PrepTM apparatus commercially available from Fluid Management Systems (FMS) Inc. (Watertown, MA, USA) which is based on the use of pressured column chromatographic procedures is an alternative to improving this step owing to its capability to process automatically unattended samples simultaneously in approx one hour. Moreover, the system reduces sample manipulation, the risks of human exposure and the costs of analysis. In the present work, we evaluated the Power PrepTM System for the analysis of PCDD/PCDF in environmental samples.

Materials and Methods

Representative sample collection, appropriate extraction techniques depending on the type of matrix as well as a standard manual cleanup based on the use of open chromatographic columns with multilayer silica, florisil, basic alumina and carbon as adsorbents were carried out as detailed in references 1,2 and 3.

The automated clean up is based on the use of multilayer silica, basic alumina and PX-21 carbon adsorbents, prepacked in teflon columns and hermetically sealed (FMS Inc., MA). The system configuration consists of a valve module, a valve drive module and a pump. All the tubes and connections in contact with the samples and solvents are made of teflon. The whole system is computer controlled and programmed as desired (eg. volume, flow rates, direction of solvent flow, etc). The pressure is also controlled by a pressure sensor on each pump module and automatically shuts the system off when it exceeds 30 psi. Further details about plumbing diagrams are given in reference 4. The previously filtered n-hexane extracts are loaded and pumped through individual sets of multilayer silica column and transferred to basic alumina column with 90 mL n-hexane at 15 mL/min. Next, the PCDD/PCDF are eluted from the alumina column and transferred to the PX-21 carbon column with 120 ml n-hexane:dichloromethane (1:1) at 8 mL/min. The interferences are eluted with 12 mL of ethyl acetate:toluene (1:1) in the forward direction at 15 mL/min, and the

PCDD/PCDF are collected in the reverse direction from the carbon columns with 65 mL of toluene at 8 mL/min.

Purified extracts were analyzed by HRGC-HRMS/EI(+)-SIM on a GC 8000 series gas chromatograph (Carlo Erba Instruments, Milan, Italy) coupled to an Autospec Ultima mass spectrometer (Micromass, Manchester, UK) equipped with a CTC A 200S autosampler, at 10000 resolving power (10% valley definition). Chromatographic separation was achieved with a DB-5 (J&W Scientific, CA, USA) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 µm film thickness) with helium as the carrier gas at a linear velocity of 35 cm/s (T: 100°C) in the splitless injection mode (1-2 µL). As a confirmation a DB-DIOXIN GC (J&W Scientific, CA, USA) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 µm film thickness) was employed when required. The temperature program was: 140 °C (1min) to 200 °C (1min) at 20 °C/min, then at 3°C/min to 300 °C and held isothermally for 20 min at 300 °C for the DB-5 GC column and 140 °C (1min) to 200 °C (1min) at 20 °C/min, then at 2°C/min to 280 °C and maintained isothermally for 85 min at 280 °C for the DB-DIOXIN GC column. Quantification was carried out by the isotopic dilution method [1-3].

Other performance checks include quality control (QC) measures: (i) continuous monitoring of laboratory contamination covering the whole analytical procedure, (ii) isomer specific GC separation, (iii) sensitivity check of MS (iv) check of MS resolution (10000), (v) sufficient recovery, (vi) parallel analysis of quality control sample and (vii) participation in interlaboratory studies.

Results and Discussion

So far, more than 300 samples have been successfully processed with the automated clean up method previously described. The system was applied to abiotic samples such as stack gas emissions, fly ash, slags, soils, ambient air and sludges.

The first step in the evaluation consisted of analyses of a standard mixture. Five different aliquots from the working standard solution formed by 17 unlabeled 2,3,7,8-substituted PCDD/PCDF from 40 to 400 pg/µL and 15 labeled 2,3,7,8-substituted PCDD/PCDF in concentrations of 100 pg/µL prepared in nonane were transferred through individual sets of 10 ml of n-hexane. The average recoveries of the native PCDD/PCDF congeners were consistently high, between 97 and 105 %, and the relative standard deviation (RSD%) ranged from 0.35 to 4.09. The recovery rates for the labeled compounds summarized in figure 1 ranged from 74 to 92 %.

Another approach was to evaluate the method against the analysis of certified materials (CRM 490). The results revealed comparable values between the data reported by BCR (3.71 ng I-TEQ/g, 7% RSD) and our results (3.24 ng I-TEQ/g, <1% RSD). Parallel analysis of control samples were also used to verify the reproducibility and the quantitative results (table 1).

In order to confirm the results of the afore-mentioned tests an congener-specific comparison of a stack emission sample cleaned up by two methods, the automated and a well-accepted standard procedure for dioxin analyses in environmental samples, was made (table 2). The results demonstrated a good correlation between the findings, with acceptable recovery rates, despite the fact that the detection limits were better with the automated system than the manual.

Table 3 gives comparison data for the levels expressed in I-TEQ and the detection limits obtained by analyzing typical environmental samples. The results reveal comparable values between both cleanup methods.

Additional evaluation of the system and quality information was obtained from participation in interlaboratory studies, such as the fourth round international intercalibration study recently organised by the Institute of Environmental Chemistry of the University of Umea, where final results are shown at this meeting [5].

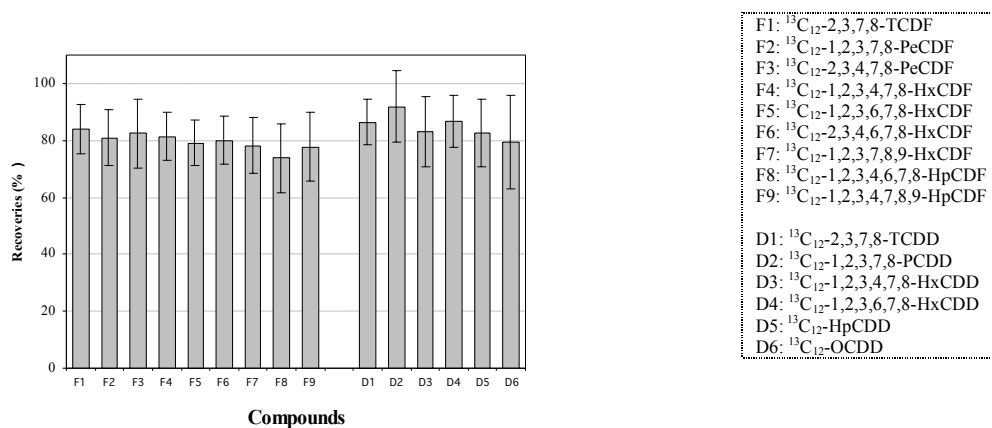


Figure 1. Internal standard recovery rates obtained by the analysis of a standard mixture.

Table 1. Parallel analysis of quality control samples.

Matrix	Aliquote 1	Aliquote 2	Aliquote 3
Flue gas emissions			
Sample 1 (pgI-TEQ/Nm ³)	87.18	85.19	-
Sample 2 (pgI-TEQ/Nm ³)	52.67	51.59	-
Fly ash			
Sample 1 (ng I-TEQ/g)	0.98	1.00	1.09
Sample 2 (ng I-TEQ/g)	3.23	3.25	3.25
Sample 3 (pg I-TEQ/g)	0.022	0.023	-
Soil			
Sample 1 (pg I-TEQ/g)	7.27	7.30	-

Table 2. Congener-specific comparison of 2,3,7,8-substituted congeners in a flue gas emission sample.

CLEANUP	Automated cleanup			Manual cleanup		
COMPOUND	Conc. (pg/Nm ³)	DL (pg/Nm ³)	¹³ C ₁₂ Recovery (%)	Conc. (pg/Nm ³)	DL (pg/Nm ³)	¹³ C ₁₂ Recovery (%)
2,3,7,8-TCDF	57,45	0,034	72	58,28	0,157	73
1,2,3,7,8-PeCDF	3,76	0,389	73	8,64	0,638	74
2,3,4,7,8-PeCDF	34,00	0,472	66	36,40	0,866	70
1,2,3,4,7,8-HxCDF	124,72	1,330	75	129,21	1,150	75
1,2,3,6,7,8-HxCDF	71,81	1,310	70	72,22	1,110	73
2,3,4,6,7,8-HxCDF	206,61	1,470	72	198,96	1,320	72
1,2,3,7,8,9-HxCDF	16,22	1,960	67	15,74	1,760	64
1,2,3,4,6,7,8-HpCDF	588,57	0,164	61	600,93	0,280	67
1,2,3,4,7,8,9-HpCDF	252,08	0,247	56	258,31	0,448	57
OCDF	1143,44	0,373		1162,02	0,412	
2,3,7,8-TCDD	0,66	0,045	75	0,25	0,188	73
1,2,3,7,8-PeCDD	2,53	0,055	73	1,95	0,226	75
1,2,3,4,7,8-HxCDD	9,21	0,169	70	9,51	0,304	65
1,2,3,6,7,8-HxCDD	24,64	0,149	70	24,86	0,268	66
1,2,3,7,8,9-HxCDD	16,06	0,160		16,96	0,287	
1,2,3,4,6,7,8-HpCDD	253,97	0,148	65	256,04	0,375	69
OCDD	769,53	0,326	55	771,73	0,455	58
I-TEQ Total (pg/Nm³)		84,64			85,51	

Table 3. Comparison data in the analysis of environmental samples cleaned up by two different methods.

Matrix	Automated clean up		Manual clean up	
	Levels*	DL	Levels*	DL
Flue gas emissions				
Sample 1 (pg/Nm ³)	94.54	0.023-2.50	99.74	0.036-3.23
Sample 2 (pg/Nm ³)	84.64	0.034-1.96	85.51	0.160-1.76
Sample 3 (pg/Nm ³)	694.67	0.016-3.13	642.33	0.085-8.38
Fly ash (pg/g)	922.19	0.006-33.2	977.2	0.004-4.40
Sludge (pg/g)	96.23	0.02-0.51	92.27	0.029-0.397
Ambient air (fg/Nm³)	50.59	0.367-13.0	46.04	0.796-34.00
Soil (pg/g)	0.40	0.010-0.11	0.42	0.004-0.051

DL: Detection Limit; * Data expressed in I-TEQ

Acknowledgments

The authors wish to thank M^a Generosa Martrat and Miguel Angel Adrados for their contribution to this work. The financial support of the Comisión Interministerial de Ciencia y Tecnología (project AMB97-0716) is gratefully acknowledged.

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